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Challenges for critical raw material recovery from WEEE

the case study of gallium

Suggested Citation
Ueberschaar, Maximilian; Otto, Sarah Julie; Rotter, Vera Susanne: Challenges for critical raw material recovery from WEEE. - In: Waste management. - ISSN: 0956-053X. - 60 (2017). - pp. 534-545. - DOI: 10.1016/j.wasman.2016.12.035. *(Postprint version is cited, page numbers may differ.)*

Abstract

Gallium and gallium compounds are more frequently used in future oriented technologies such as photovoltaics, light diodes and semiconductor technology. In the long term the supply risk is estimated to be critical. Germany is one of the major primary gallium producer, recycler of gallium from new scrap and GaAs wafer producer. Therefore, new concepts for a resource saving handling of gallium and appropriate recycling strategies have to be designed.

This study focus on options for a possible recycling of gallium from waste electric and electronic equipment. To identify first starting points, a substance flow analysis was carried out for gallium applied in integrated circuits on printed circuit boards and LED used for background lighting in Germany in 2012. Moreover, radio amplifier chips (integrated circuits) were investigated in detail to deduct first approaches for a recycling of such components. An analysis of recycling barriers was carried out in order to investigate general opportunities and risks for the recycling of gallium from chips and LED.

Results show, that significant gallium losses arose during the production and the waste management. 93 ± 11 %, equivalent to 43,000 ± 4,700 kg of the total gallium potential were lost over the whole process until applied in electronic goods. The largest share of 14,000 ± 2,300 kg gallium was lost in the primary production process. The refining process was connected to additional 6,900 ± 3,700 kg and the chip and wafer production to 21,700 ± 3,200 kg lost gallium. Due to low collection rates, further 400 ± 200 kg of gallium were not recycled. Due to the fact, that no recycling of gallium from WEEE exists, all gallium is lost in the current waste management system.

A thermal pre-treatment of the chips, followed by a manual separation allowed an isolation of gallium rich fractions, with mass fractions up to 35 %. Here, gallium loads per Chip were between 0.9 and 1.3 mg. Copper, gold and arsenic were determined as well. The pyrometallurgical copper route might be an option for gallium recycling. A recovery of gold and gallium in combination with copper is possible due to a compatibility with this base-metal. But, a selective separation prior to this process is necessary. Diluted with other materials, the gallium content would be too low and the recovery not feasible any more.

The recycling of gallium from chips applied on printed circuit boards and LED used for background lighting is technically complex. Recycling barriers exist over the whole recycling chain. A forthcoming commercial implementation is not expected in nearer future. This applies in particular for gallium bearing chips.

Keywords: Recycling, recovery, critical metals, gallium, Waste Electric and Electronic Equipment (WEEE), substance flow analysis (SFA), material flow analysis, recycling barriers

1. Introduction

Due to its content of highly functional and strategically important metals Waste Electric and Electronic Equipment (WEEE) has been recently discussed as an upcoming source for raw materials. In the same time "recycling restrictions" are one of the key indicators for classifying metals as critical (European Commission, 2014, 2010). The present economic and legal boundary conditions result in recycling technologies that are not optimized for the recovery of all materials, in particular not for minor metals. As a consequence, recovery of critical metals from WEEE is, in opposite to the recovery of industrial base and precious metals, limited in current practice.

The project UPgrade aims at an enhanced recovery of trace metals along the value chain by developing new liberation and separation processes (mechanical, thermal, chemical), considering the technological requirements of final recovery processes. "Upgrading" material flows along the recycling chain does not aim at a 100% recovery of all metals, but is the result of an interdisciplinary decision making and optimization inside recycling networks.

Main drivers for current recycling are the recovery of valuable materials like precious metals (silver, gold), platinum group metals (palladium, platinum) and bulk materials like industrial base metals (copper, steel/iron, aluminium) and plastics. These materials can be used as indicators for measuring the efficiency of current recycling processes and have been defined as "lead metals". Additionally, cadmium and lead are metals of environmental concern which need to be addressed in the recycling chain of WEEE. Approaches developed in the UPgrade project focus on both, lead and target metals in order to establish higher recycling rates of critical elements in combination with economically feasible processes. Figure 1 shows an overview of all addressed metals investigated in this project.

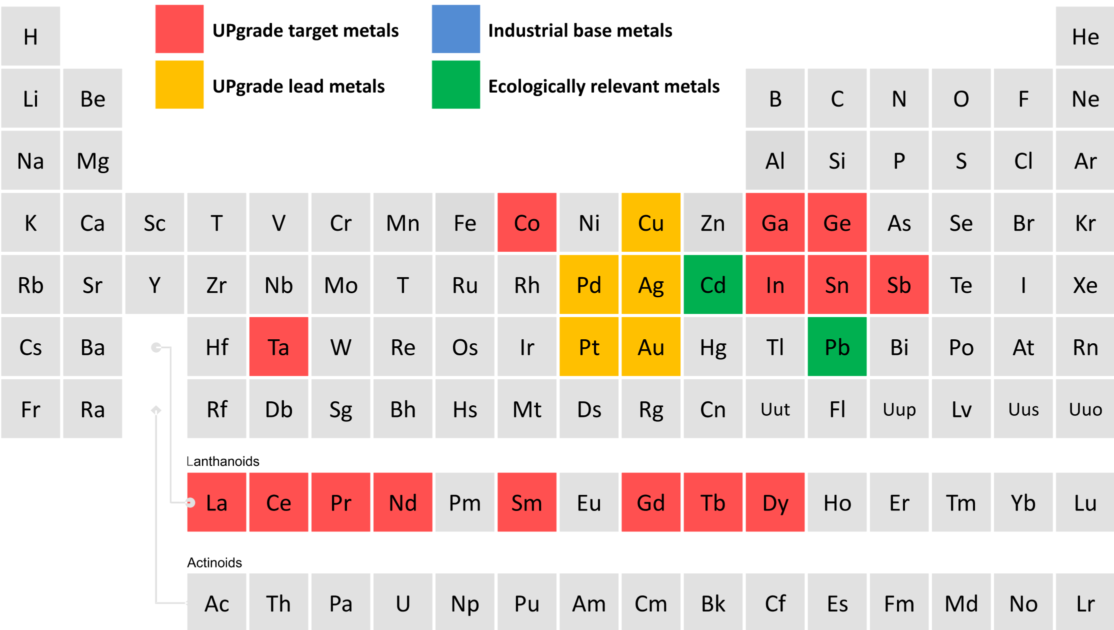

Figure 1: Defined target, lead and other investigated metals within the UPgrade project

This article presents selected results for the particular case of gallium. We want to assess gallium flows in primary production and waste flows related to WEEE with a material flow analysis (MFA). Through this, losses and according recycling potentials related to location and relevance will be identified. In addition, a first approach for the pre-treatment of gallium bearing components will be investigated for its selectivity. Finally, we want to identify potential recycling barriers, which hampers or support the recycling of gallium based on the findings in this study.

2. Background

2.1. Primary production of gallium

Approximately 90 % of produced primary gallium is extracted as a by-product of the aluminium production (Zhao et al., 2012). Most important primary resource is the mineral bauxite, which is used for both, the aluminium and gallium production (Angerer et al., 2009). The Ga content in bauxite ranges from 0.0025 to 0.01 % (Schreiter, 1960). Therefore, even refined aluminium can contain between 0.017 % and 0.02 % of gallium. With current processing strategies, approximately 70 % of the gallium potential can be extracted; 30 % remain in the red sludge (Zhao et al., 2012).

Other potential gallium resources are zinc sulfides, respectively by-products of zinc smelting processes. Gallium in low thermal native zinc sulfides can be present with mass fractions up to 0.002 % (Schreiter, 1960). Up to 3 % of the globally available gallium originates from this source (Løvik et al., 2016). Moreover, minor concentrations of gallium can be measured in some coal deposits. But, processes for an extraction from coal or fly ashes with reasonable expenses are not developed yet (Løvik et al., 2016; Wittmer et al., 2011).

In 2014, 444 Mg gallium have been extracted worldwide (U.S. Geological Survey, 2015). Regarding the refining process, China and Germany had a share of 54 % and 13.5 %, respectively (Drobe and Killiches, 2014). But, the production and demand is rapidly increasing. Between 2009 and 2011, the production of extracted and refined gallium doubled (Dehnavi, 2013). This was most probably based on the growing market of general wireless communication and mobile technologies, which are using gallium based power amplifier. This is intensified by higher sales of LED used as background lighting and in lighting industry in general. Estimations reaching till 2050, forecast a demand 12 times higher for gallium (Løvik et al., 2016).

2.2. Use and application of gallium

GaAs, GaA, GaP and GaSb are the most generally applicated gallium semi-conductor compounds (Roskill, 2012). But almost 99 % of the produced gallium is applied in form of GaAs and GaN (Jaskula, 2014).

The main end-use-sector of Gallium is in the Electric and Electronic Equipment (EEE) sector being approx. 90 % of the total production. Inside the EEE sector, almost 68 % of the applied gallium is needed for integrated circuits, which are required for high-frequency wireless communication (e.g. mobile phones – 4G, 3G, 2G, etc. or WLAN). The remaining material is mostly used for opto-electronic components like LED or laser diodes for background lighting in computers, TV, mobile phones or photodetectors and solar panels (Jaskula, 2014). An overview of the Ga consumption worldwide in 2012 is shown in Table 1.

Table 1: Share and amount of the worldwide Ga-consumption per end-use-sector (Roskill, 2012)

End-use-sector	**Share in 2014**	**Consumption in 2012**
	[%]	[t]
Integrated circuit and field-effect transistors	50	177
LED for background and general lighting applications	38	135
Photovoltaics	4	14
Other	8	28

This study focuses on the application of gallium in the EEE sector. Recent studies from Chancerel et al., 2015, 2013 or Oguchi et al., 2011 highlight the relevant equipment types from information and telecommunications equipment (IT) and consumer equipment, which were investigated in detail (cf. Table 2).

Table 2: Relevant WEEE categories for GaAs potential (Chancerel et al., 2013; Oguchi et al., 2011)

Category	Investigated equipment type	UNU key
Investigated equipment with gallium on printed circuit boards	Desktop PC	0302
	Notebook	0303
	Printer	0304
	Mobile phone	0306
	Video Cassette Recording (VCR)	0404
	DVD-Player	0404
	Radio/Recorder	0403
	Digital camera	0406
	Video camera	0406
	Video games	0702
Investigated equipment with gallium in LED for background illumination	Notebook	0303
	TFT-TV	0408
	Flat screen monitor	0309

2.3. Recycling

According to the UNEP - International Resource Panel, 2011, the functional end-of-life recycling rate of gallium is under 1 %. Primary reason is the application of this element only in minor mass fractions in relevant equipment types. First recycling approaches for single components like LED are presented by Swain et al., 2015 or Rotter et al., 2016b. Yet, in general recycling processes, gallium is usually further diluted and subsequently lost. Due to this, gallium is classified as not recyclable (Ciacci et al., 2015).

Currently, a recovery is carried out only for material streams with high gallium mass fractions. These concentrates arise only in the processing of semi-finished products in form of processing residues, mainly coming from GaAs wafer production. About 45 % of the gallium input in the production originates from this new scrap. (U.S. Geological Survey, 2015)

2.4. MFA of gallium

The material flow analysis has been introduced as a systematic approach to track goods, materials and substances to understand the origin and fate in investigated processes (Brunner and Rechberger, 2004). Only a few MFA studies were carried out for gallium. Most recent studies were presented by Dehnavi, 2013; Licht et al., 2015; Løvik et al., 2015 and Zimmermann, 2016. While Zimmermann, 2016 focus on CIGS, all other studies depict the global gallium flows in the production and partially for the waste management for the year 2010 or 2011. The provided overall quantities give a first indication of recycling hotspots, but in order to deduct concrete recycling strategies, more detailed information is needed. This applies in particular for the waste management.

3. Material and Methods

3.1. Material Flow Analysis Gallium

3.1.1. System boundaries and system description

For carrying out a material flow analysis, the lifecycle of gallium was split into three sub-systems, namely “production”, “use” and “waste management” (cf. Figure 2). The use phase is not considered in this MFA. The systems “production” and “waste management” were modeled individually, since the major gallium share from production is exported as semi-finished products and most gallium bearing products are imported.

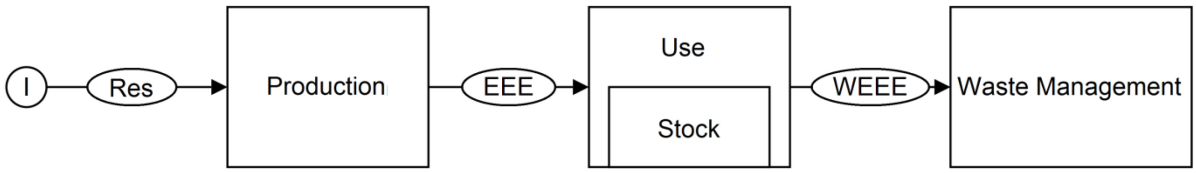

Figure 2: Lifecycle of gallium (Res = primary resource)

As regional system and time boundary we chose Germany with reference year 2012. The focus is set on IT and entertainment equipment containing gallium bearing PCB or LED (cf. Table 2). Not all data, necessary for calculating needed transfer coefficients are available for this year. Subsequently, we used approximated and fitted data from other years.

As there is no current recycling of gallium from WEEE, the system ends with the waste management and is not reconnected to the production side. Only recycling efforts in the production processes feed back directly within the production system. Supportive information S2.4.1 shows the detailed qualitative material flow model of the system „production", which is used for further modeling. It contains five process steps that are linked to each other, wherein the sink represents the sum of all losses. The model starts with the primary resource potential (Res) of gallium in bauxite, which is related to efficiencies of status-quo processes. Here, losses (primary waste: PW) are transferred to the red mud (cf. supportive information S2.2.1). The extracted gallium (primary gallium: PG) is then refined to obtain desired purities (cf. supportive information S2.2.2). Losses through refining waste (RefW) are summed up in the “sink production”.

Germany has only low refining capacities (Roskill, 2012). The process itself is not bounded to a specific location (Wittmer et al., 2011). This leads to considerable import and export masses. The import constitutes the major source of refined gallium for Germany. The export is dominated by unrefined material (cf. supportive information S2.1) (Liedtke, 2015). These mass flows are not part of the model, as only a potential from self-supply was investigated.

The refined gallium (RG) is then transferred to the producing industry and applied in wafers (W), which are passed on to the chip producing industry for further processing steps. In addition to losses in both steps (WW and CW), the wafer production generates a recyclate (R) as a by-product, which can be recycled subsequently to secondary gallium. This material is fed to the refining processes of gallium. A final semi-finished product represents the output from the subsystem “production”. Supportive information S2.2 provides more detailed information for this subsystem.

The system “production” includes another sub-system named “processing industry” (see supportive information S2.4.2). Here, one individual system was developed based on the wafer and chip production to harmonize various existing processes with fluctuating losses. So far, only in the production of wafers, a recycling of new scrap takes place without considering CIGS solar panels.

Supportive information S2.4.3 depicts the system “waste management”, which refers to all relevant IT and entertainment equipment types (cf. Table 2). This sub-system starts right after the use phase of EEE. In order to apply an appropriate recycling, WEEE is collected by public waste management authorities, distributers and manufacturers which share the product responsibility (Bundesministerium für Umwelt Naturschutz Bau und Reaktorsicherheit, 2015). Here, first losses occur due to low collection rates of relevant devices. The collected material is then pre-processed by means of manual and mechanical treatment. Printed circuit boards (PCB) represents the major carrier of gallium and are therefore characterized as a concentrate (C). The separation process of these components is related to losses, basing on low efficiencies in the sorting processes or losses through dust during a mechanical treatment. Pyrometallurgical processes are used for the recovery of metals in PCB. Here, an extraction of gallium is possible but not executed yet. Therefore, no recovery flows of gallium are included in this system. Like in the system “production”, the sink is the sum of all losses.

The system “waste management” differentiates between the WEEE streams, which are officially collected and the transfer to the informal sector. But due to inconsistent and fragmentary background data, the waste flows in the informal sector are not part of this study. Supportive information S2.3 provides more information for the subsystem “waste management”.

3.1.2. Data collection and processing

The quantitative determination of required data can follow two different methodical approaches. Process input and output flows can be determined by literature research or they can be calculated by using more general transfer coefficient, if no specific data is available. These two approaches were used complementary in this study. Data on transfer coefficients were collected by literature research, expert consultations and reasonable assumptions (cf. supportive information S2.2).

Furthermore, uncertainties in the data sets have been considered and an error propagation has been applied. As the data sources for this MFA are heterogeneous, they should not be used in an equivalent way. Following Laner et al., 2015, sources have been rated regarding their reliability and according uncertainties have been set up (c.f. Table 3).

Table 3: Data sources for the MFA and the according uncertainties used for error propagations

Source	**Uncertainty**	
Concrete indication of quantities from reliable sources	10 %	Very low
Official statistical reports (e.g. federal environmental agency, Roskill reports, etc.) or quantifications for transfer coefficients based on expert interviews or scientific articles	20 %	Low
Conversion of data	50 %	Medium
Assumptions	60 %	High

3.1.3. Modelling

The MFA model with flow calculation and data reconciliation was carried out using the software STAN, which is developed by the Institute for Water Quality, Resource and Waste Management of Vienna University of Technology. A normal distribution was considered, although this assumption could not be verified due to limited data. The uncertainties were expressed as standard deviation. Under given normal distributed data, the software enables compensation of data, identification of false data and calculation of unknown quantities and error propagation.

3.2. Technical approaches for the recovery from gallium bearing components

Three different state-of-the-art IC used for mobile radio standards like 2G, 3G, 4G or WLAN were investigated in detail. Those components are generally applied in modern smartphones, mobile phones, tablets, etc. Table 4 shows the properties of the components and the investigated quantities. For example pictures of the samples, see supportive information S3.1. All chips consist of labeled synthetic material at the front and a metal plate at the back. The area is less than 1 cm^2 for all chips. Supportive information S3.2 depicts the single weights of the samples.

Table 4: Amount and details of investigated radio chips

Chip-Type	Manufacturer	Model no.	Specifications	Average weight	Number of samples
Type 1	TriQuint	TQM7M9053	Quad-band GSM-EDGE and Tri-Band W/CDMA/HSPA+/LTE	86±2 mg	4
Type 2	TriQuint	TQM7M5012	Quad-Band GSM850/GSM900/DCS/PCS Power Amplifier Module	61±0.3 mg	3
Type 3	Skyworks	SKY77544	Quad-Band GSM / GPRS / EDGE – Triple-Band WCDMA	81±0.1 mg	2
Total	-	-			9

Pre-tests showed, that no manual, mechanical nor chemical liberation of single components was possible. Therefore, a thermal treatment was applied. The samples were heated at 250° C for 110 minutes and again at 550° C for 360 minutes in a muffle furnace. With this procedure, the plastics casings were burned and the inboard components were liberated. The thermal exposure revealed single modules, which were clearly separable (cf. supportive information S3.3). For a subsequent chemical analysis, the liberated components have been sorted according to visual identifiable characteristics like form or color. Four clusters were identified:

(1) Isolation with copper connectors
(2) Metal plates (back of the chip)
(3) Electronic modules (chip)
(4) Others

All fractions were weighted and chemically analyzed with an X-Ray fluorescence analysis (XRF) (Thermo Fisher/ Analyticon XL3 Air) to determine the chemical composition. The samples were measured several times from various angles without any further processing to avoid losses related to milling and decanting.

3.3. Analysis of recycling barriers

In order to evaluate potential opportunities and risks for the recycling of gallium from printed circuit boards (chips) and LED used for backlighting, an analysis of barriers, which support or limit the recycling of gallium has been carried out following (Rotter et al., 2016a, 2015). Here, all boundary conditions regarding product related properties, available and used technology for liberation, separation and refining of the material as well as economic parameters were considered. Supportive information S4 shows the investigated parameter.

4. Results & discussion

4.1. MFA gallium

4.1.1. Material flow model of the system “production”

This model consists of five processes, while one process represents the losses occurring during the primary production of gallium and the further processing. In 2012, 32,000 ± 3,200 kg of gallium were extracted as a by-product of the aluminium production (cf. Figure 3). Only 70 % of the gallium potential is extracted from the lye in the Bayer process. Through this, 14,000 ± 2,300 kg gallium remain in the red mud and is subsequently landfilled. This represents the highest loss in the system ‘production’ (cf. supportive information S2.2.1).

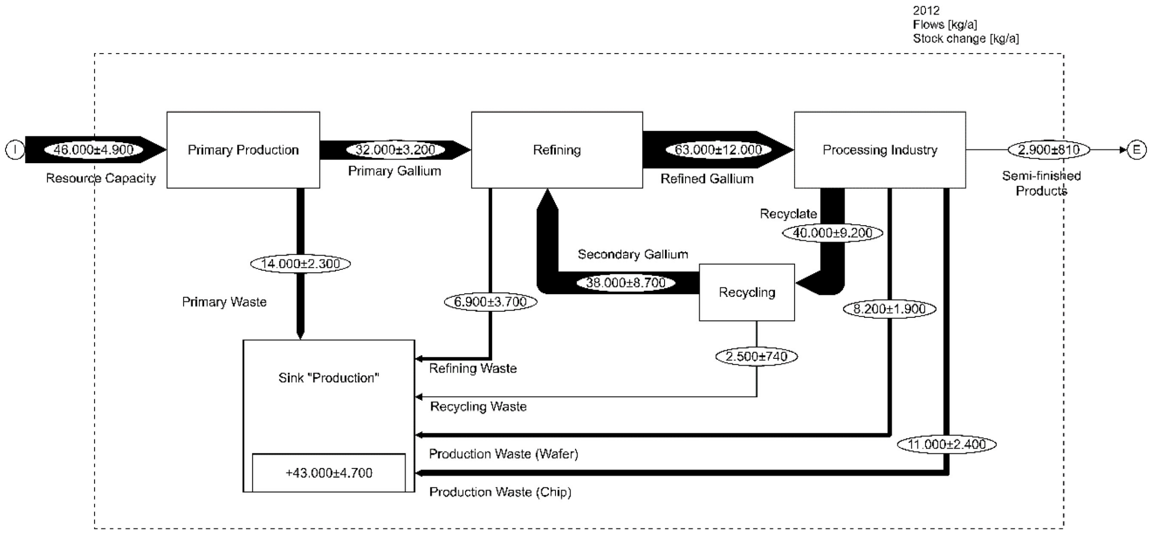

Figure 3: Quantitative material flow model of the system "production" for gallium

In order to concentrate and to obtain required grades, the gallium is subsequently refined (cf. supportive information S2.2.2). Here, the refining losses are much smaller with 6,900 ± 3,700 kg. From the refining step, about 63,000 ± 12,000 kg of gallium is transferred to the processing industry. This increased amount of gallium is subjected to recycled new scrap, which arises mainly in the wafer production. This material can be recycled and is led back to the refining process. This saves 38,000 ± 8,700 kg of the containing gallium. Here, only 3 %, i.e. 2,500 ± 740 kg are lost during the recycling. This is the lowest quantity of lost gallium in the system “production”.

Figure 4 shows the subsystem “processing industry” (cf. supportive information S2.2.3). Two of the four output flows depict losses, which are assigned to the wafer production (cf. supportive information S2.2.4) and to the chip production (cf. supportive information S2.2.5). In the chip production process, the substrate thickness must be reduced or partially removed. Here, a high concentrated gallium material is lost. This flow accounts to 11,000 ± 2,400 kg of a total of 14,000 ± 3,000 kg transferred into this process. Herewith, the losses in the chip production are comparable to the losses in the primary production of gallium.

Although a high percentage of the production waste is recycled after the wafer production, about 8,200 ± 1,900 kg gallium are not recovered. In total, only 8 % of the refined gallium is applied in electric and electronic products in form of chips.

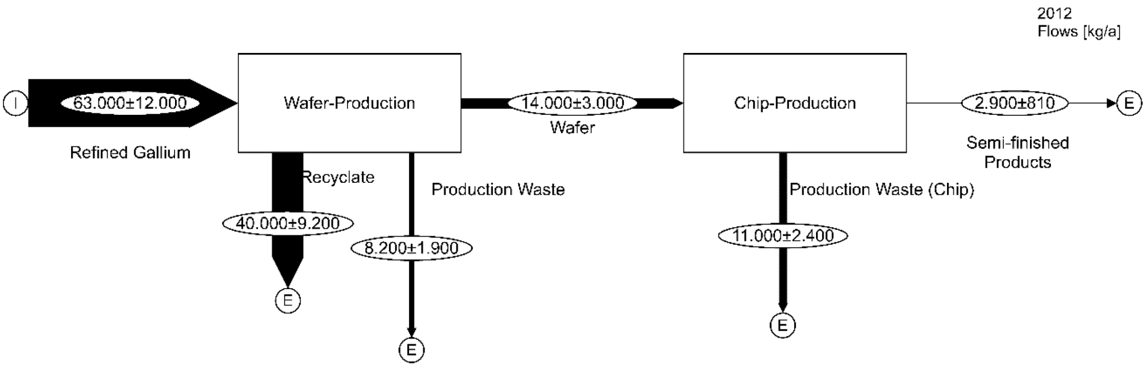

Figure 4: Quantitative material flow model of the sub-system "processing industry"

In 2012, the system “production” had a total loss of 43,000 ± 4,700 kg, which is 93 % of the total gallium input. These flows are supposed to be transferred to e.g. landfills as red mud, which represent a stock. As stock transfers prior to 2012 are not known, this study shows only the change in stock. For a direct comparison, Figure 5 shows the relative values.

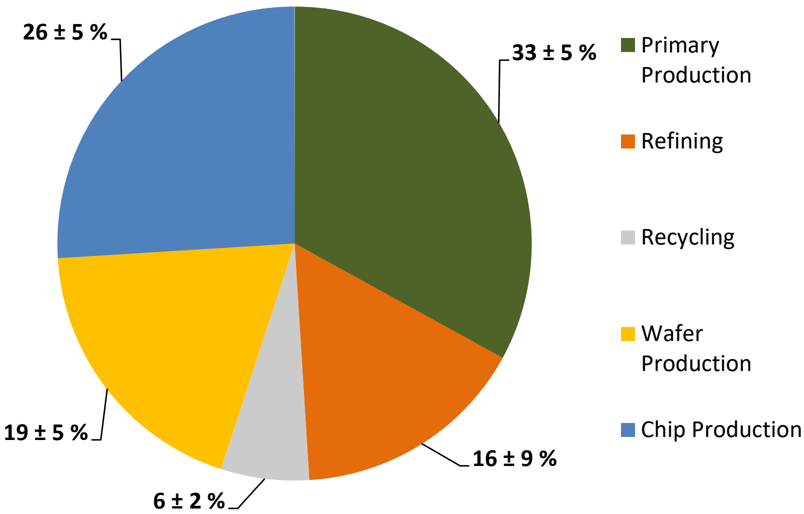

Figure 5: Relative shares of all gallium losses in the system “production”

The highest losses with 33 ± 5 % occur during the primary production of gallium, followed by the chip production with 26 ± 5 % and wafer production with 19 ± 5 %. Only low losses are assigned to the refining process (16 ± 9 %) and the recycling of the new scrap (6 ± 2 %).

4.1.2. Material flow model of the system “waste management”

Major losses within the system “waste management” base on an insufficient collection of arising WEEE (cf. Figure 6). Not collected WEEE is assigned to losses over residual waste collection, at home stored end-of-life devices and a transfer of WEEE into the informal sector (cf. supportive information S2.3.1).

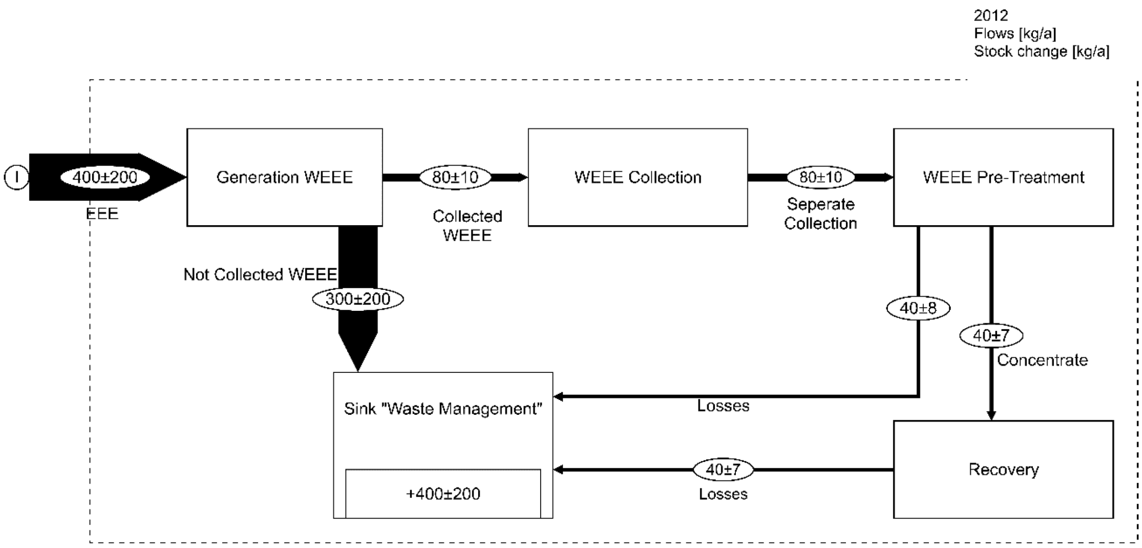

Figure 6: Quantitative material flow model of the system "waste management"

All flows in this system were determined individually for PCB and LED bearing devices. Figure 7 illustrates the gallium amounts referring to the gallium bearing PCB applied in the investigated equipment types in WEEE. In Germany in 2012, over 400 kg gallium arise with the generation of WEEE. About 340 kg of this potential was not collected. Major part constitutes of mobile phones with a share of over 280 kg. Only almost 80 kg gallium was collected through the formal collection of end-of-life devices.

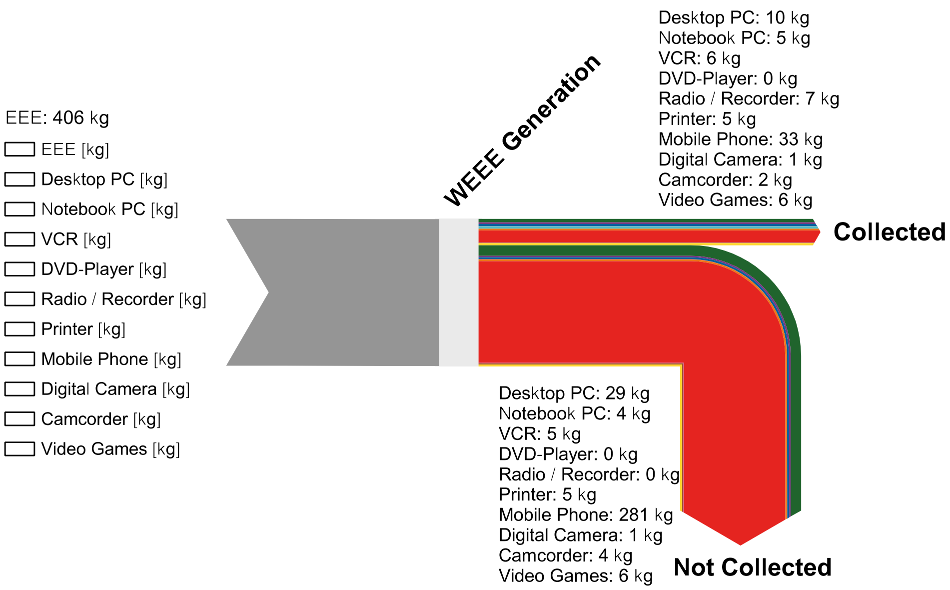

Figure 7: Collected and not collected gallium amounts with PCB in WEEE

For gallium flows related to LED, applied as background lighting in WEEE screen devices, the differences between the investigated equipment types are not as high as for gallium flows related to PCB. Results for the three investigated device types are depicted in Figure 8. Here, a total of almost 10 kg arises with WEEE in one year. The losses range from 1.3 kg to 2.5 kg gallium.

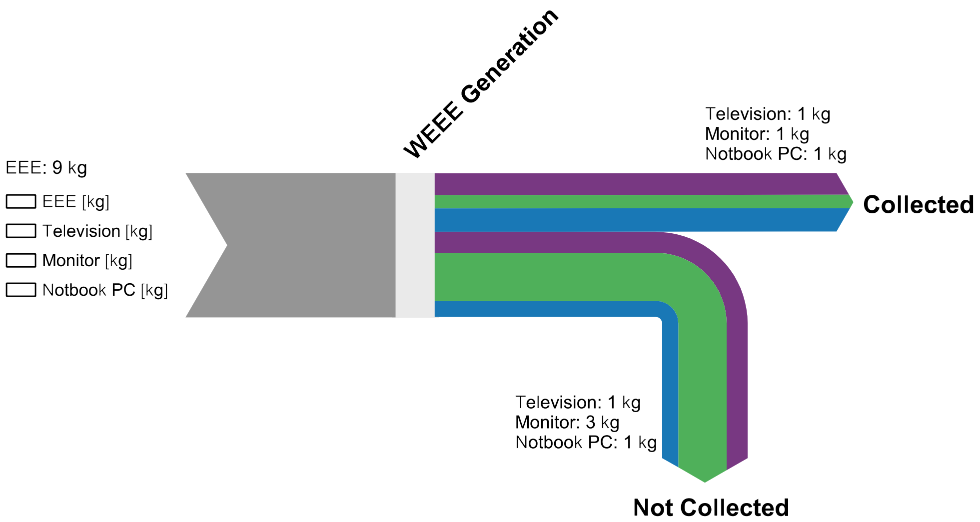

Figure 8: Collected and not collected gallium amounts through LED used for background lighting in WEEE

The total amount of collected PCB and LED related gallium sums up to almost 80 kg. Figure 9 shows the distribution according to the investigated equipment types. Mobile phones clearly account the major share with 43 % of the total gallium collected with WEEE, followed by desktop PC (14 %). All other equipment types have a share less than 10 % each.

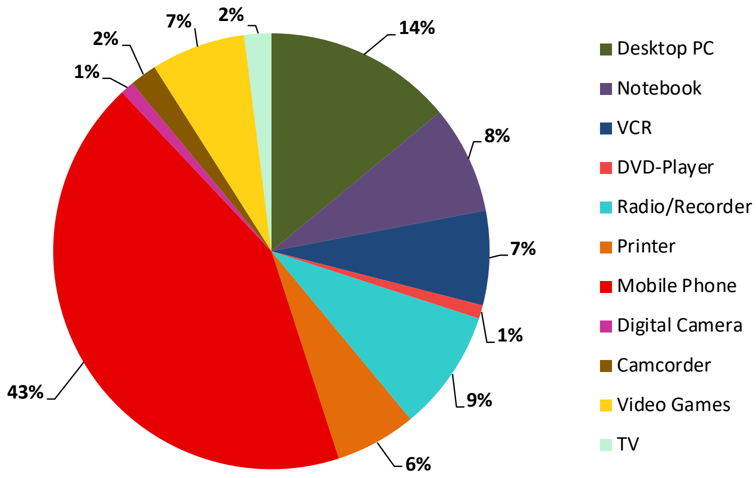

Figure 9: Share of gallium related equipment types in collected WEEE

Figure 10 and Figure 11 show the gallium flows for the relevant equipment types with applied PCB or LED within the treatment of WEEE (cf. supportive information S2.3.2, S2.3.3 and S2.3.4). Here, Figure 10 shows the flows of collected gallium from PCB, Figure 11 for gallium from LED for background lighting. After the collection step, all material is directed to a manual pre-treatment, followed by mechanical processing. Here, losses are assigned to an incorrect sorting of the PCB and dust discharges in general. Subsequent to the pre-treatment, recyclates are further processed with metallurgical approaches in order to recover single metals. The used pyrometallurgical processes are not optimized for a recovery of gallium. Through this, gallium is not concentrated as a single output and 100 % of the gallium input is lost. So far, only one process is known from Umicore. But here, gallium is recovered only from CIGS solar modules.

Figure 10 shows, that the highest gallium losses related to PCB are assigned to mobile phones with 13 kg. All other investigated equipment types account for 0.3 kg to a maximum of 5 kg lost gallium. Since no gallium in WEEE is recycled the sum of the losses is the same as the input into the system "waste management".

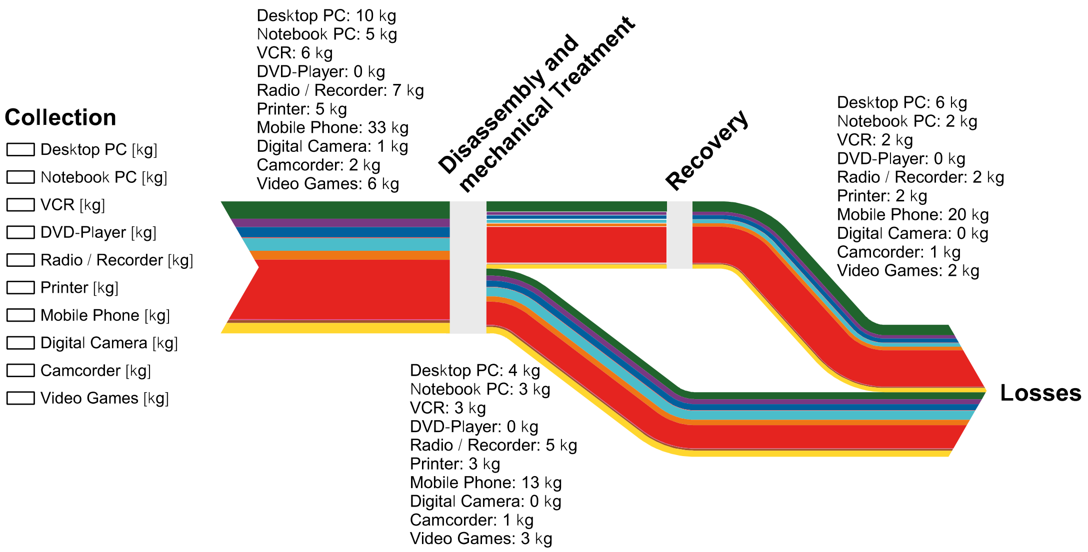

Figure 10: Flows of collected gallium from PCB in the treatment of WEEE

In total, 40 ± 8 kg gallium is lost during the manual disassembly and the mechanical treatment. This is almost the same amount, which is lost during the metallurgical processes.

In contrast to the PCB treatment, no gallium containing concentrate for LED is generated after the disassembly or mechanical treatment, which leads to complete loss at this stage (Figure 11). The sum of the LED loss is 3.7 kg and is also here the same as the input in this system.

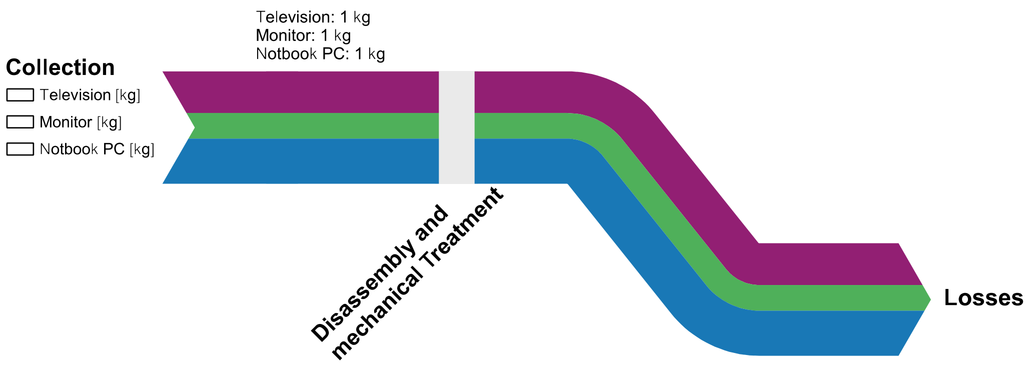

Figure 11: Flows of collected gallium from LED in the treatment of WEEE

The cumulated gallium losses in the system "waste management" related to LED and PCB sum up to 400 ± 200 kg. Figure 12 shows the relative proportions. Here, WEEE collection accounts almost 80 % of the total losses. WEEE treatment is related to lower losses, although no gallium is recovered here.

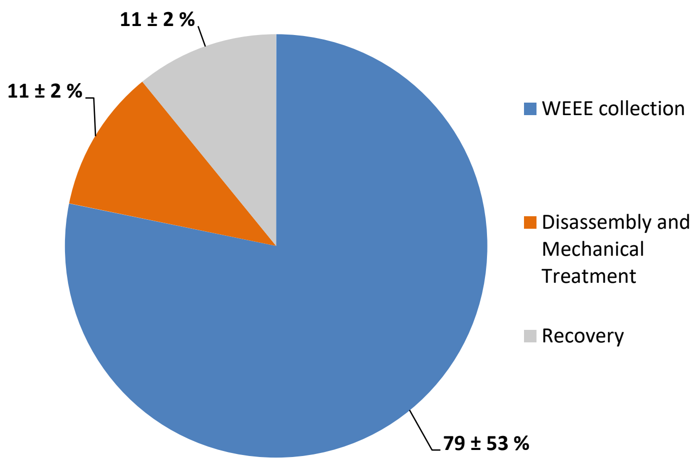

Figure 12: Relative proportions of the losses related to the system "waste management"

4.2. Technical approaches for the recovery from gallium bearing components

Table 5 describes the physical properties of the chips. The inner structure is very complex, varying for each chip type.

Table 5: Physical and mechanical properties of investigated chip-types

Properties		Type 1	Type 2	Type 3
Dimension	**Weight [mg]**	85	61	82
	Length [mm]	7.5	5	6
	Width [mm]	5	5	6
	Thickness [mm]	0.9	1	0.9
Stability	**Untreated**	Very stable	Very stable	Very stable
	After thermal treatment	Easily removable fractions	Moderately removable fractions	Easily removable fractions
Loss of weight	**Due to thermal treatment [%]**	14.4	8.7	11.6
	Due to separation and decanting [%]	6.1	5.5	3.3
No. of fractions after sorting process	**Isolation with copper connections**	1	1	1
	Metal plate (back of the Chip)	1	1	1
	Electronic module	1	1	5
	Other	1	1	-

4.2.1. Liberation and separation with thermal treatment

Table 6 shows the obtained sorting fractions after the thermal treatment and the assigned sample numbers, which are used for a further description.

Table 6: Designation of the isolated fractions

	Isolation with copper connections	Metal plate (back of the Chip)	Electronic Module	Other

Type 1	T1-1	T1-2	T1-3	T1-4
Type 2	T2-1	T2-2	T2-3	T2-4
Type 3	T3-1	T3-2	T3-3 *[T3-3.1, T3-3.2, T3-3.3, T3-3.4, T3-3.5]*	-

Figure 13 depicts exemplary the sorting fractions of chip type 1 and 2. Type 3 is optically similar to the first type. Red circles mark single components with unlikely appearance, which were categorized to the most probable fraction.

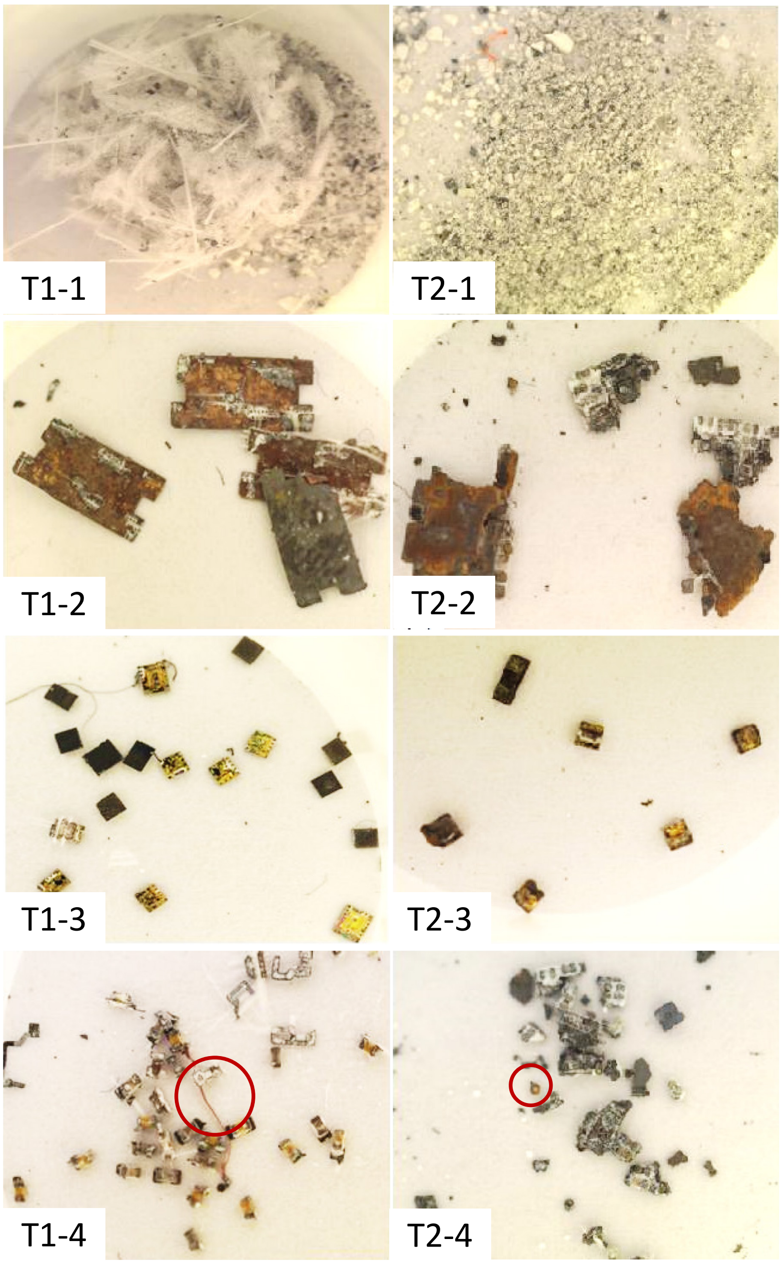

Figure 13: Comparison of the liberated fractions from chip type 1 and type 2

4.2.2. Determination of chemical composition with XRF analysis

Results of the chemical analyses showed a mixture of various elements, including high shares of precious metals in some fractions. Here, six most relevant elements according to their mass shares and economic significance were chosen to be investigated in more detail. Those are copper, gallium, germanium, arsenic, silver and gold. Figure 14 shows the results for each sample in detail (cf. supportive information S3.4).

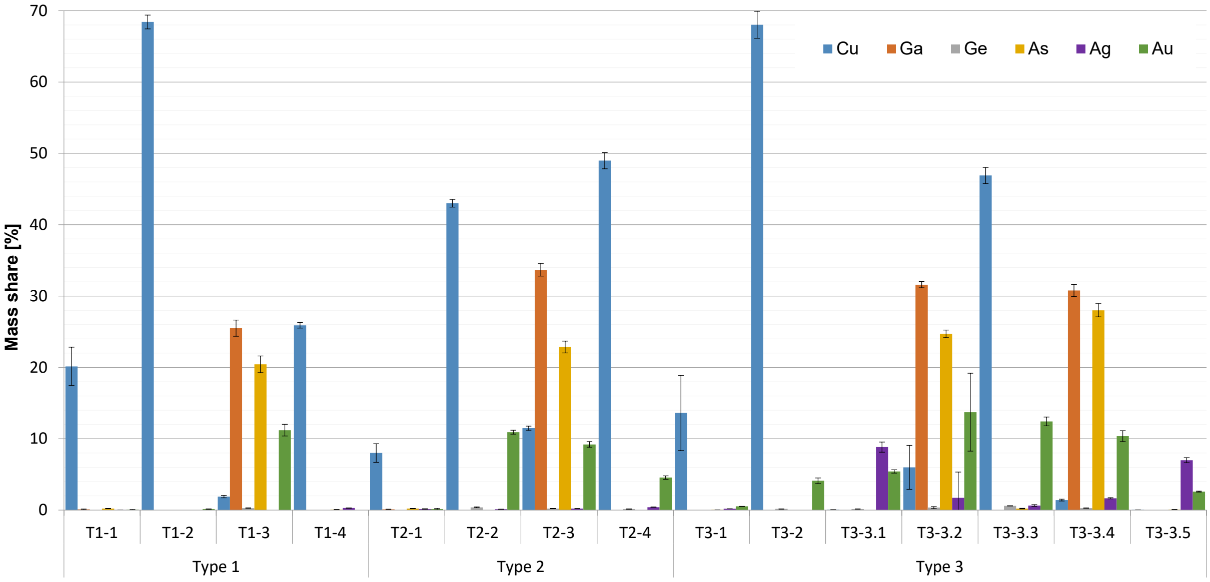

Figure 14: Mass fractions of Cu, Ga, Ge, As, Ag and Au in the separated components of the three investigated radio chips

In each IC chip, at least one fraction holds a gallium mass share between 25 and 32 %, but also a share 20 to 28 % of arsenic. In all chips, this applies for the "electronic component" fraction, in which gallium and arsenic is applied in a similar ratio. In six fractions, gallium was detected, four had higher mass fractions, from which two fractions were found in chip type 3.

Another critical element, which is also defined as target metal in the UPgrade project is germanium. Germanium was found in 9 of 15 fractions in very low concentrations ranging from 0.15 to 0.6 %.

Highest copper loads were found in the metal plate on the back of each chip (T1-2, T2-2, T3-2), while a smaller amount was applied in the isolation with copper connectors (T1-1, T2-1, T3-1).

Gallium and arsenic can be assigned to particular sorting fractions. Furthermore, the results prove the possibility of concentrating gallium and arsenic with the tested approach. In all investigated chips, the GaAs rich fractions were assigned to "electronic modules", which can be recognized by its light golden glimmer. Besides gallium, this fraction contains economically valuable metals like gold or copper. Here, further studies must evaluate a combined recovery of these applied metals.

Based on the weights of the fractions and the determined mass fractions of applied elements, potential loads of target metals have been calculated (cf. Table 7). These results are only approximate values, as the measurement accuracy of the used XRF technique is limited.

Table 7: Loads of Cu, Ga, Ge, As, Ag and Au and total mass of chip in mg per unit

	Total chip	**Cu**	**Ga**	**Ge**	**As**	**Ag**	**Au**
	Load in mg						
Type 1	85	15.3	1.3	<0.1	1.2	<0.1	0.6
Type 2	61	12.9	1.8	<0.1	1.3	0.1	2.3
Type 3	82	12.9	0.9	<0.1	0.8	0.3	1.2

No significant differences were determined for copper loads in the investigated chips. Copper constitutes the most applied metal in all investigated chips, followed by the sum of gallium and arsenic. In type 3, the gallium and arsenic load is much lower, whereas the gold load is higher compared to type 1. In two of three chips the mass of gold content is higher than the load of gallium.

4.3. Analysis of recycling barriers

Results obtained from the recycling barrier analysis were converted into a SWOT diagram to depict opportunities and risks for the recycling of gallium from chips applied on PCB and LED in a comprehensive way. Each application is assessed in a single analysis. The SWOT analysis for chips is depicted in Table 8, LED is shown in Table 9.

The relatively small shares of gallium bearing components in PCB or LED leads to a dilution with other material in conventionally applied recycling processes. Ending in the pyrometallurgical process for copper and precious metals refining, gallium is transferred oxidized to the slag. Based on this, gallium rich components must be separated prior to any mechanical processing with other material. In particular mobile phones and newly tablets are important gallium sources, bearing more than 40 % of the total gallium loads in the IT and entertainment equipment.

This study proves a liberation and separation of gallium containing components in IC. Relevant components with high gallium shares were separated. This material must be treated subsequently for a selective isolation of gallium from the copper, gold matrix. Arsenic as a contaminant has to be investigated in detail as well.

Table 8: SWOT-analysis of gallium recycling from IC chips applied on PCB

	Strengths		**Weaknesses**					
Opportunities	Probably increasing collection rates	High potential in mobile phones	First approaches for treatment of chips tested	Other radio technologies are available, increasing substitution of Ga by e.g. silicon-based technologies		Currently, relevant devices are collected in insufficient quantities		Currently, no recycling channels available
Threats	Recycling conflicts with gold and copper	IC and LED are main applications of Ga	Complex design of chips	No identification technology for chips available	No explicit labelling for doping elements	Gallium applied as trace metal, arsenic as contaminant for metallurgy	Material value low	Energy and chemicals consumption for thermal and chemical processing increasing for low grade input

Other studies in UPgrade showed a possible approach for the treatment of LED (Rotter et al., 2016b). Here, an isolation of the chip from the converter material, which contains rare earth elements was executed. A concentration of gallium is possible as well. These results will be published in a forthcoming paper.

Table 9: SWOT-analysis of gallium recycling from LED

	Strengths	**Weaknesses**

Opportunities	No significant change in product design of LED is forthcoming	Screen devices are disassembled for de-contamination reasons, LED fraction as by-product	First approaches for treatment of LED tested in UPgrade	Probably increasing collection rates	Currently, relevant devices are collected in insufficient quantities	First approaches for treatment of chips tested in UPgrade	Currently, no recycling channels available
Threats	Change in lighting technologies like shift to OLED	Identification visually possible, but no automatization available yet	Recycling conflict with gold and copper	IC and LED are main applications of Ga	Gallium applied as trace metal, partially arsenic as contaminant for metallurgy	Material value low	Energy and chemicals consumption for thermal and chemical processing increasing for low grade input

5. Conclusion

Currently, a recycling of gallium applied in WEEE could not cover the needs for the production of new EEE products. In Germany in 2012, 2,900 ± 810 kg gallium was supplied in form of semi-finished products. In contrast, only about 400 kg gallium arose with the obsolescence of EEE, from which only about 80 kg were collected with the general collection of WEEE. Gallium is not recovered in current WEEE recycling processes. Moreover, a recycling from post-consumer waste is not expected in a short or middle term perspective.

Nevertheless, the recycling of gallium from WEEE is technically feasible. Yet, due to the design and use of gallium bearing components, various process steps are required. In particular the identification and separation of according components is complex. But, the use of gallium is limited to only a few applications, which might facilitate such processes. Material flows of similar components could be combined to supply larger mass flows to recycling facilities. This study proves the technical possibility of liberation and separation of gallium concentrates. Selected subsequent processes would enable the recovery of gallium and other valuable materials like gold and copper. This combines economical and ecological requirements for developing recycling strategies for critical raw materials.

Yet, major losses of gallium occur not in the waste management, but rather in the production of gallium bearing components. In Germany in 2012, losses in various process steps summed up to 43,000 ± 4,700 kg, which is 93 % of the total gallium input. The largest share is related to the primary production, due to transfers of gallium to the red mud. Therefore, recycling strategies for gallium from red mud and optimized processes for the gallium extraction bear major opportunities to reduce gallium losses and to improve efficiencies. Other high losses are assigned to the chip and wafer production. Here, focus should be set on the optimization of the waste water treatment.

Funding

This work was funded by the German Federal Ministry of Education and Research (BMBF) (UPgrade - Project reference number 033R087A)

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Supportive information

Challenges for critical raw material recovery from WEEE - the case study of gallium

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S1 Data collection

The mass flow analysis for gallium in the systems production, processing industry and waste management is based on many scattered data, which has to be harmonized. Many data sets are very difficult to access or do not even exist so that assumptions or data conversions were made based on different sources. Depending on the reliability and accuracy of original data to be transferred into the model, uncertainty must be determined and used for further calculations. Table 1 shows all required data for the development of the gallium MFA model for all investigated systems.

Table 1: Required data for the gallium MFA for each investigated system

System	Process	Required data
Production	Primary production	- Production capacity - Amount of the obtained primarily raw gallium - Losses during production
	Refining	- Input amount of raw gallium in process (from primary and secondary production) - Amount of refined gallium - Losses during refining processes
	Processing industry	- Input amount of refined gallium - Amount of gallium in finished chips for use in electrical equipment - Losses during processing - Amount of recyclable materials from production residues
	Recycling	- Input amount of gallium to be recycled - Losses during recycling - Amount of recycled gallium
	Sink	- Input streams consisting of losses of all processes in the system production
Processing industry	Wafer production	- Input amount of refined gallium - Losses due to production waste - Amount of recyclable materials from production residues - Amount of gallium finally applied in wafer
	Chip production	- Input amount of gallium in wafer - Losses during production processes - Amount of gallium in finished chips for use in electrical equipment
Waste management	Generation of WEEE	- Mass fractions of gallium in WEEE devices - Amount of gallium available for recycling through formal collection of WEEE - Amount of gallium in not collected WEEE
	Collection	- Mass of collected gallium containing WEEE devices - Amount of gallium, which enters pre-processing of WEEE
	Pre-processing of WEEE	- Input amount of gallium - Losses during pre-processing - Gallium amounts in processed and sorted metal concentrates for further recycling steps
	Further processing / end-refining	- Input amount of gallium in metal concentrates - Gallium losses during further recycling steps - Amount of gallium recovered during further processing steps / end-refining
	Sink	- Input streams from losses of all processes in the system “waste management”

S2 Data base

S2.1 Import and export of gallium

Table 2: Import quantities of gallium in Germany in 2012

Country	Import [kg]	Share of total import [%]
Belgium	700	2.1
China	3,000	8.98
France	100	0.3
Great Britain	14,600	43.71
Netherlands	100	0.3
Slovakia	11,900	35.63
Ukraine	100	0.30
USA	2,900	8.68
Total	33,400	100

Based on (Liedtke, 2015)

Table 3: Export quantities of gallium in Germany in 2012

Country	Export [kg]	Share of total export [%]
Australia	100	0.25
Great Britain	9,400	23.38
Italy	100	0.25
Japan	100	0.25
Korea	100	0.25
Luxembourg	100	0.25
Austria	100	0.25
Poland	1,300	3.23
Sweden	100	0.25
Switzerland	4,500	11.19
Singapore	100	0.25
Slovakia	100	0.25
Slovenia	100	0.25
USA	24,000	59.70
Total	40,200	100

Based on (Liedtke, 2015)

S2.2 Data base for system “production”

S2.2.1 Primary production of gallium

Germany represents one of the major producers of primary, secondary and generally refined gallium (USGS, 2016). INGAL Stade, which is owned by Molycorp (50 %) and 5N plus (50 %), is main producer of primary gallium in Germany (Roskill Information Services, 2014). The production capacity is 35 t/a (Liedtke, 2015). In 2012, 32 t were produced (Roskill Information Services, 2014). Only approximately one third of the actual potential of gallium in bauxite is extractable (Liedtke, 2015). Primary production processes from lye originating from the Bayer process as input material transfer 70-80 % of this extractable potential to refining processes. The remaining 20-30 % are disposed to the red mud (Zhao et al., 2012).

S2.2.2 Refining of gallium

The purity is highly important for the application of gallium in electronic goods. Raw gallium usually has a purity between 99.0 % and 99.9 %. For the further use as semi conductors in semi-finished products, purities of 99.9999 % (6N) up to 99.999999 % (8N) are needed (Ullmann’s Encyclopedia, 2012). For this, refining processes separate present impurities. The recovery of gallium chloride from acid solutions and fractional distillation of liquid gallium represents one option. Higher purities are obtained by fractional crystallization, zone melting, or single crystal growth (Løvik et al., 2015; Moskalyk, 2003; Ullmann’s Encyclopedia, 2012). Zone melting represents one of the most effective procedures (Ghosh et al., 2009). Depending on the process, various losses occur. Due to impurities, edges are cut and discarded after the zone melting process. In these residues, small amounts of gallium may be present. In the single crystal growth process, gallium can be transferred to the remaining melt. (Wittmer et al., 2011)

Germany has insufficient refining capacities. Almost the entire produced primary gallium in Stade as well as the secondary material from the processing industry in Germany are shipped abroad to the United States and the United Kingdom (Liedtke, 2015).

Only PPM Pure Metals in Langelsheim is refining gallium. In 2013, the capacity of refined gallium was 10 t/a. This value is taken for further calculations in the MFA model. An according uncertainty was determined (cf. original study). (Roskill Information Services, 2014)

Refining is related to losses, depending on the origin of the material (primary, secondary source), used refining processes, and further unspecified losses. For this, no concrete data is available. Therefore, an assumption of 1 % was adopted for this MFA, originating from (Dehnavi, 2013).

S2.2.3 Processing of refined gallium

In Germany, refined gallium is used mainly for further processing in microelectronics and to a certain extend as wafer in optoelectronics (Liedtke, 2015). Companies, that handle gallium are listed in Table 4.

Table 4: Companies processing gallium in Germany

Company	Products
Freiberger Compound Materials	Mainly GaAs wafer
Osram Opto Semiconductors	GaAs, InGaN, InGaIP, Wafer for LEDs
AZZURRO Semiconductors	GaN on silicon epitaxialwafer for LEDs
BOSCH	CIGS
Centrotherm Photovoltaics	CIGS
Solarion	CIGS
Solibro (Hanergy)	CIGS
Würth Solar GmbH & Co KG	CIGS

Based on (Roskill Information Services, 2014)

One of the world's largest producers of compound semiconductor substrates for micro- and optoelectronics is the Freiberger Compound Materials (FCM) in Freiberg/Germany. In this study, the authors assume, that most of the current gallium flows enter here (Liedtke, 2015). FCM contributes a share of 37 % of the total GaAs substrates supply for the world market (Roskill Information Services, 2014).

S2.2.4 Wafer production

The refined gallium is then entering the processing industry, in which it is processed to GaAs for example by means of arsenic high-pressure synthesis followed by crystal growth. Sawing and etching processes combined with subsequent polishing and cleaning steps lead to the finished wafer. Through this, process residues arise, which are differentiated in two kind of material streams. From some of these residues, gallium can be recovered. Therefore, they represent recycling streams in this study. Gallium in other streams are irretrievable lost. 60 % of the gallium input is transferred to the process residues in the wafer production. 18 % gallium, originating from scraps from crystal growing, sawing and etching processes, and 30 % in form of mud are re-directed to recycling processes. This sums up to 48 %. The remaining 12 % are lost through waste water, respectively remains in the arsenic containing precipitation sludge from the subsequent waste water treatment. In the recycling processes, about 3 % gallium is lost through process residues. Therefore, 45 % are redirected to the wafer production process (Stelter and Zeidler, 2013). FCM covers about 40-50 % of its input with this secondary gallium.

S2.2.5 Chip production

Significant losses of gallium take place in the last step of the production chain. Process residues from substrate processing and chip production cannot be recycled to recover gallium. These residues are generated while reducing the substrate thickness after the epitaxial layers have been produced. Partially, a complete removal is conducted for the production of specific LED. Through this, only about 8 % of the total used gallium is applied in final EEE products (Stelter and Zeidler, 2013).

Wafer production takes place mainly in the production of microelectronics and to a small extend in the production of optoelectronics. Wafer, produced by FCM in Germany, are usually exported. Further processing is carried out in Asian countries. The final components are then assembled in the USA as there is no market for this in Germany (Liedtke, 2015).

OSRAM Opto Semiconductors GmbH produces semiconductors for LED mainly for own needs. But, the manufacturing of the end product takes place in Malaysia. (OSRAM Opto Semiconductors, 2015)

AZURRO semiconductors was a relatively small company with 42 employees in 2012 with headquarters in Dresden. In 2014, AZURRO stopped the production and registered their insolvency. They were specialized in the field of wafer production for LED and power electronics. (ALLOS Semiconductors, 2015)

S2.3 Data base for system "waste management"

S2.3.1 WEEE collection

The system "waste management" starts with the obsolescence of EEE. Yet, not all generated WEEE is collected with formal collection systems. The calculation of these losses bases on extrapolations and reasonable assumptions. Due to a general lack of data, figures from 2007 are used and might differ to the data in 2012 (Chancerel, 2010). Comparisons for single devices for different years revealed only low differences (Manhart et al., 2012). Differences to the actual collection data gives indication for losses (stiftung elektro-altgeräte register, 2015).

In Germany, WEEE is collected and grouped in collection groups (CG). The CG and the related collected masses in Germany in 2012 are displayed in Table 5.

Table 5: Collection of CG 3 and 5 in Germany in 2012

<table>
<tr><th rowspan="3">Collection group</th><th rowspan="3">Device categories</th><th rowspan="2">Put-on-market</th><th colspan="4">Collection</th></tr>
<tr><th>Private households</th><th>Other sources</th><th>Total category</th><th>Total Collection group</th></tr>
<tr><th>[t]</th><th>[t]</th><th>[t]</th><th>[t]</th><th>[t]</th></tr>
<tr><td>CG 3</td><td>IT and telecommunication</td><td>248,878</td><td>137,045</td><td>23,080</td><td>160,125</td><td rowspan="2">331,479</td></tr>
<tr><td>CG 3</td><td>Entertainment electronics</td><td>180,767</td><td>160,299</td><td>11,055</td><td>171,354</td></tr>
<tr><td>CG 5</td><td>Lighting products without gas discharge lamps</td><td rowspan="2">67,711</td><td>445</td><td>136</td><td>581</td><td rowspan="2">10,260</td></tr>
<tr><td>CG 5</td><td>Gas discharge lamps</td><td>8,455</td><td>1,224</td><td>9,679</td></tr>
</table>

Based on (Umweltbundesamt, 2015)

The CG consist of various device types. Table 6 shows the clusters of further considered devices per CG.

Table 6: Clustering of investigated devices

Equipment group	Considered devices
Mobile phones	Mobile phones
Desktop PC	Desktop PC
CRT monitor	-
Large high-grade equipment	DVD player, video games / consoles, TFT monitors, notebooks PC, Printer, VCR
Small high-grade equipment	Digital cameras, camcorder
Low-grade equipment	Radio / recorder

Based on (Chancerel, 2010)

The share of the considered devices was deducted from various sources. Table 7 depicts the shares of VCR, DVD-player and radios in CG 3. Table 8 shows the shares of printers, digital cameras, camcorder and video games / consoles in CG 3 and CG 5.

Table 7: Share of VCR, DVD-player and radio / recorder in CG 3

Device	Collected units	CG 3 total	Share of CG 3
	[-]	[t]	[%]
VCR	7,300	1.936	1
DVD-Player	760		0.1
Radio/Recorder	9,700		1.7

Based on (Technische Universität Berlin, 2014)

Table 8: Share of electrical appliances in SG 3 and SG 5

Device	Share of CG 3	Share of SG 5
	[%]	[%]
Printer	6,1	
Digital camera	0,1	-
Camcorder		
Video games / consoles	0,51	

Based on (stiftung elektro-altgeräte register, 2015; Technische Universität Berlin, 2014)

For further calculations, the average unit weights are needed. Table 9 shows the average masses of the investigated devices.

Table 9: Weight mapping per piece depending on the device type

Device	UNU key	Average weight
		[kg/unit]
Desktop PC	0302	8.8
Notebook PC	0303	3
VCR	0404	2.7
DVD player	0404	2.7
Radio / recorder	0403	3.4
Printer	0304	10
Mobile phone	0306	0.1
Digital camera	0406	0.3
Camcorder	0406	0.3
Video games / consoles	0702	1.9

Based on (Baldé et al., 2015)

Gallium in PCB containing devices

Oguchi et al., 2011 examined the share of PCB in various WEEE devices. The mean values are used for further calculations. Table 10 shows the share of PCB for each device and the according gallium mass fraction in the PCB.

Table 10: Share of printed circuit boards and their levels of gallium in WEEE

Device	Share of PCB	Mass fraction of gallium in PCB
	[%]	[mg/kg]
Desktop PC (n=5)	11.7	11
Notebook PC (n=10)	15.6	10
VCR (n=18)	18.7	9
DVD player (n=4)	14.1	9
Radio / recorder (n=18)	10.4	12
Mobile phone (n=16)	29.5	140
Digital camera (n=2)	20.3	15
Camcorder (n=2)	17.7	52
Video games (n=2)	20.6	16

The equation used for the calculation of gallium losses for PCB bearing devices is depicted in Equation 1.

Equation 1: Calculation of gallium losses for PCB bearing devices

$$Ga_{coll.}[kg] = \sum mCG[kg] * S_{\frac{Device}{CG}}[\%] * S_{\frac{PCB}{Device}}[\%] * S_{\frac{Ga}{PCB}}[\frac{mg}{kg}]$$

With:

$Ga_{coll.}$ = Gallium collected with Ga containing screen devices in kg; mCG = mass of WEEE per collection group in kg; $S_{Device/CG}$ = share of PCB containing devices in collection group in %; $S_{PCB/Device}$ = share of PCB in device in %; $S_{Ga/PCB}$ = mass fraction of gallium in PCB in mg/kg

Gallium in LED containing devices

The calculation of gallium in LED bearing devices considers TFT TV, PC monitors and notebooks. The collected masses in 2013 are depicted in Table 11.

Table 11: Collected amounts of screen devices in CG 3 in Germany in 2013

Device	Collected mass
	[t]
TFT TV	5,000
PC monitors	7,500
Notebooks	3,000

Based on (Rotter et al., 2015)

An estimation of the number of applied LED per device builds the basis for the calculation of the total gallium masses per device. Only white LED are considered, as gallium is mostly used for this type (Buchert et al., 2012). In 2010, in about 30 % of LCD TV and monitors as well as in 90 % of notebooks, LED were applied for background lighting (Buchert et al., 2012). Table 12 shows the estimated LED amounts of LED per device.

Table 12: Estimated LED amounts per device

Device	Amount of white LED per device	Amount of gallium in semiconductor chip of one LED
	[-]	[µg]
Notebooks	50	32.5
PC monitors	100	
TFT TV	150	

Based on (Buchert et al., 2012)

The equation used for the calculation of gallium losses for LED bearing devices is depicted in Equation 2.

Equation 2: Calculation of gallium losses for LED bearing devices

$$Ga_{coll.}[kg] = \sum \frac{mSD_{per\ type}[kg] * S_{Devices\ with\ LED}[\%]}{m_{Device}[kg]} * \#LED * mGa_{LED}[kg]$$

With:

$Ga_{coll.}$ = Gallium collected with Ga containing screen devices in kg; $mSD_{per\ type}$ = Mass of all collected screen devices per type in kg; $S_{Devices\ with\ LED}$ = Share of devices using LED as background lighting in %; m_{Device} = Average weight of screen device in kg; #LED = Number of white LED per device; mGa_{LED} = Gallium load per LED in [kg]

Gallium losses in WEEE collection

With this data basis, gallium masses related to PCB and LED in WEEE is calculated. Table 13 shows the resulting losses of gallium due to not collected WEEE related to PCB.

Table 13: Losses of gallium due to not collected WEEE containing PCB

Device	Not collected masses	Not collected units	Not collected gallium masses	Share
	[t]	[-]	[kg]	[%]
Desktop PC	22,624	2,570,954	29	8.7
Notebook PC	2,891	963,757	4,5	1.4
VCR	3,267	1,209,953	55	16.5
DVD player	339	125,600	0,5	0.2
Radio / recorder	-1,517	-446,239	-1.9	-0.6
Printer	20,091	2,009,054	4,8	1.4
Mobile phone	6,808	68,083,682	280,8	84.3
Digital camera	775	2,582,991	1.2	1.1
Camcorder			3.6	
Video games / console	1,680	884,053	5.5	1.7
TV	4,819	892,867,173	-	-
Total	61,777	78,876,173	333	100

Table 14 shows the not collected gallium masses for LED containing WEEE.

Table 14: Losses of gallium due to not collected WEEE containing LED in background lighting

Device	Not collected masses	Not collected units	Amount of not collected LED	Not collected gallium masses	Share
	[t]	[-]	[-]	[kg]	[%]
TFT TV	4,819	892,367	267,710	1.3	25
PC monitor	22,624	2,570,954	771,286	2.5	48
Notebook	2,891	963,757	867,381	1.4	27
Total	30,334	1,856,199	1,906,377	5.2	100

The overall calculated share of collected and not collected WEEE in Germany in 2007 is shown in Table 15.

Table 15: Calculated share of collected and not collected WEEE in Germany in 2007

Equipment group	Generated WEEE	Collected	Not collected
	[t]	[t]	[%]
Mobile phones	2.273	239	89
Desktop PC	39.957	9.948	75
CRT monitor	200.000	134.126	33
Large high-grade equipment	87.071	44.339	49
Small high-grade equipment	2.550	764	70
Low-grade equipment	93.513	127.938	-37
Total	425.364	317.354	25

S2.3.2 WEEE pre-processing

WEEE processing considers dismantling and mechanical treatment. Chancerel et al., 2010 examined the routes and fates of gold and palladium in WEEE processing. As gallium is applied mostly in the same devices, the transfer coefficients were used for this study. Table 16 depicts the losses of precious metals in WEEE pre-processing

Table 16: Losses of precious metals in WEEE pre-processing

Equipment group	Losses
	[%]
Mobile phones	39
Desktop PC	40
CRT monitor	40
Large high-grade equipment	60
Small high-grade equipment	60
Low-grade equipment	71

Based on (Chancerel et al., 2010)

Gallium losses in pre-processing of PCB containing devices

Table 17: Gallium losses in pre-processing of PCB containing devices in Germany in 2012

Device	**Lost gallium**
	[kg]
Desktop PC	3.9
Notebook PC	2.8
VCR	3.4
DVD player	0.3
Radio / recorder	5
Printer	3
Mobile phone	12.9
Digital camera	0.3
Camcorder	0.9
Video games / console	3.5
TV	-
Total	35.8

Gallium losses in pre-processing of LED containing devices

Table 18: Gallium losses due to pre-processing of LED containing devices in Germany in 2012

Device	**Lost gallium**
	[kg]
TFT TV	1.4
PC monitors	0.8
Notebooks	1.5
Total	3.7

S2.3.3 Further WEEE processing

Table 19: Gallium losses in further recycling steps of PCB in Germany in 2012

Device	Lost of gallium [kg]
Desktop PC	5.8
Notebook PC	1.9
VCR	2.3
DVD player	0.2
Radio / recorder	2.0
Printer	2.0
Mobile phone	20.1
Digital camera	0.2
Camcorder	0.6
Video games / console	2.3
TV	-
Total	37.3

S2.3.4 WEEE end-refining

Umicore recovers gallium from CIGS scrap in special recycling routes only (Oosterhof, 2011). Other end-refiners like Boliden, Aurubis or Remondis generally do not recover gallium, neither from PCB nor from LED. CIGS are not part of this study. Due to this, 100 % of gallium from WEEE is lost in the end-refining.

S2.4 Qualitative material flow models

S2.4.1 Qualitative material flow model of the system “production"

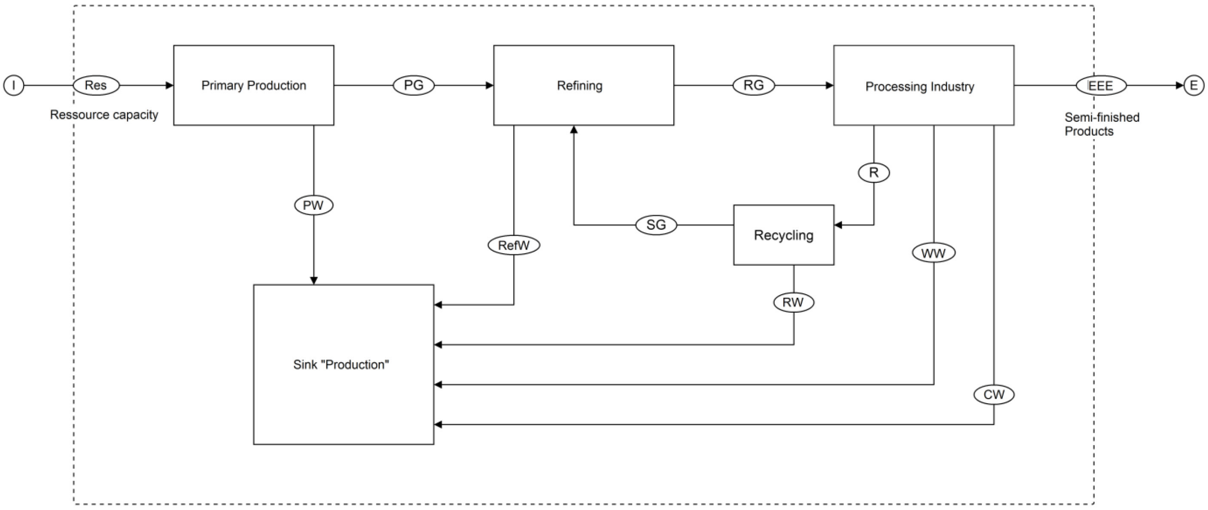

Figure 1: Qualitative material flow model of the gallium “production" system (PG: primary Ga, RG: refined Ga, R: Recyclate, SG: secondary Ga, PW: primary production waste, RefW: refining waste, RW: recycling Waste, WW: production waste (Wafer), CW: production waste (chip)

S2.4.2 Qualitative material flow model of the sub-system “processing industry"

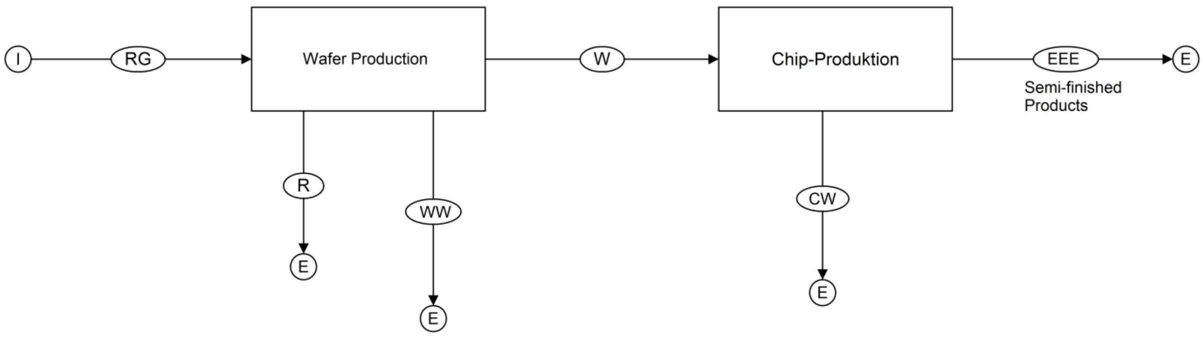

Figure 2: Detailed scheme of the sub-system "processing industry" (RG: refined Ga, W: wafer, R: recyclate, WW: wafer waste, CW: chip waste)

S2.4.3 Qualitative material flow model of the system “waste management"

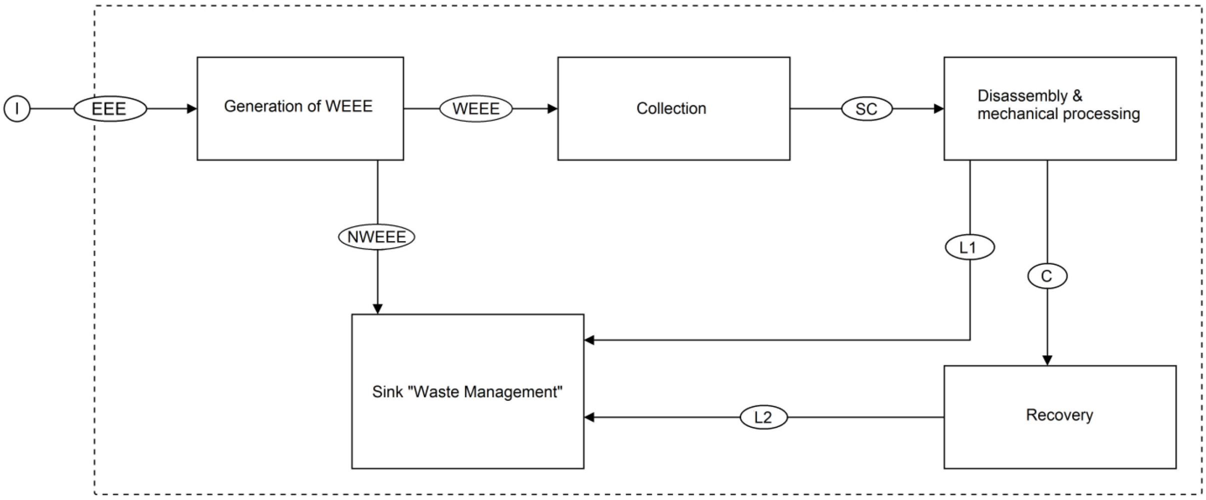

Figure 3: Qualitative material flow model of the system "waste management"(NWEEE: not collected WEEE, SC: separate collection, C: concentrate, L1 and L2: losses)

S3 Thermal treatment of IC

S3.1 Example pictures of IC chips

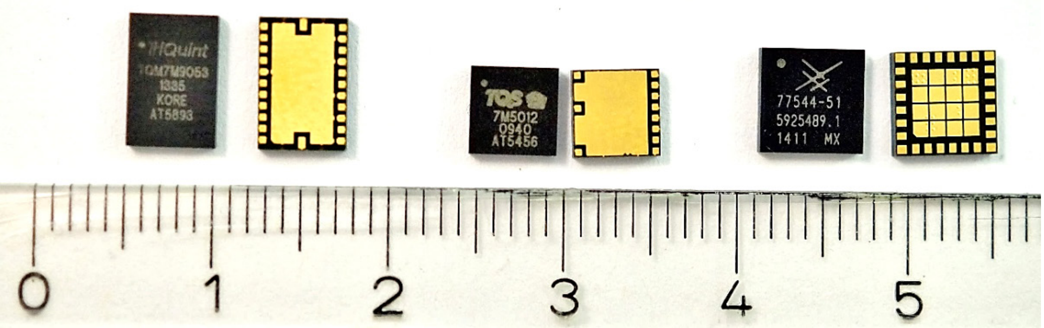

Figure 4: Overview of investigated chip types (from left to right: Type 1, Type 2, Type 3)

S3.2 Weights of IC samples

Table 20: Weights of investigated chips

Chip Nr.°	Weight [mg]		
	Type 1	Type 2	Type 3
1	88.3	61.2	81.4
2	84.4	60.8	81.5
3	85.9	60.6	-
4	84.3	60.8	-
Total	337.9	243.4	162.9

Table 21: Weight losses of chips after thermal treatment

Chip Nr.°	Losses due to thermal treatment [%]		
	Type 1	Type 2	Type 3
1	14.4	8.7	11.8
2	14.8	8.7	11.4
3	14.1	8.6	-
4	14.5	8.9	
Average	14.4	8.7	11.6

S3.3 Output fractions from thermal treatment

The thermally treated IC were separated into 4 different fractions: 1) isolation with copper contacts, 2) metal plate (back of chip), 3) electronic components (chip), 4) miscellaneous

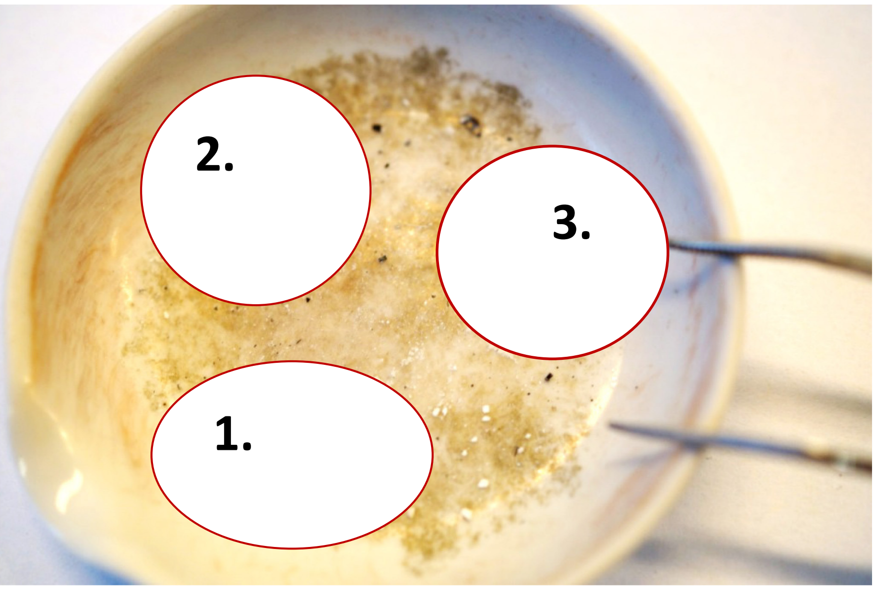

Figure 5: Liberated and sorted components of a high-frequency radio chip after thermal treatment

S3.4 Chemical analyses of output fractions

Table 22: Number of XRF measurements

Probe	Cu	Ga	Ge	As	Ag	Au
T1-2	5	-	-	-	-	5
T1-4	5	-	-	5	5	-
T1-1	5	5	-	5	4	4
T1-3	5	5	5	5	-	5
T2-2	5	-	5	-	5	5
T2-3	5	5	5	5	5	5
T2-1	5	5	-	5	5	5
T2-4	5	-	5	-	5	5
T3-3.1	5	-	5	-	5	5
T3-3.2	5	-	5	5	5	5
T3-3.3	5	5	5	5	5	5
T3-3.4	5	-	2	-	3	5
T3-3.5	5	-	-	5	2	5
T3-3.6	5	5	5	5	5	5
T3-3.7	4	-	-	5	5	5

Table 23:Chemical analyses results of all IC fractions after thermal treatment

Sample	Cu	Ga	Ge	As	Ag	Au
	[mg/g]					
T1-2	684±10	-	-	-	-	14±0.3
T1-4	260±4	-	-	0.7±0.1	3±0.1	-
T1-1	200±30	1±0.5	-	2.2±0.2	0.14±0.03	0.5±0.4
T1-3	19±2	250±11	3±0.3	200±12	-	110±8
T2-2	430±6	-	4±0.6	-	1.2±0.1	110±3
T2-3	115±3	340±9	2.1±0.2	230±8	2±0.1	90±4
T2-1	80±10	1±0.2	-	2.2±0.1	1.5±0.3	1.5±1
T2-4	500±10	-	1.6±0.2	-	4.1±0.1	46±2.5
T3-3.1	0.6±0.07	-	1.5±0.1	-	100±7	55±2.3
T3-3.2	60±30	320±4	3.5±1.4	250±5	17±40	140±55
T3-3.3	500±11	-	6±0.3	2.1±0.3	6.5±1	120±6
T3-3.4	700±20	-	1.6±0.1	-	-	40±4
T3-3.5	140±53	-	-	0.4±0.1	2±0.02	5±0.2
T3-3.6	14±1.3	310±8	3±0.1	280±9	17±1	100±8
T3-3.7	0.42±0.01	-	-	0.7±0.1	70±3	26±0.6

Table 24: Cu, Ga, Ge, As, Ag, and Au in mg

Sample	Cu	Ga	Ge	As	Ag	Au
	[mg]					
T1-2	12.9	-	-	-	-	0.03
T1-4	5	-	-	0.01	0.06	-
T1-1	43	0.2	-	0.5	0.03	0.1
T1-3	0.4	5.2	0.06	4.1	-	2.3
T2-2	16	-	0.2	-	0.05	4
T2-3	1.8	5.4	0.03	3.7	0.03	1.4
T2-1	5.9	0.08	-	0.2	0.1	0.1
T2-4	14.8	-	0.05	-	0.1	1.4
T3-3.1	0.001	-	0.004	-	0.2	0.1
T3-3.2	0.2	1	0.01	0.7	0,05	0.4
T3-3.3	1.4	-	0.02	0.01	0.02	0.4
T3-3.4	8.6	-	0.02	-	-	0.5
T3-3.5	15.6	-	-	0.04	0.2	0.6
T3-3.6	0.04	0.8	0.01	0.8	0.05	0.3
T3-3.7	0.001	-	-	0.001	0.1	0.03
Total type 1 (n=4)	61.2	5.4	0.06	4.6	0.09	2.4
Total type 2 (n=3)	38.6	5.5	0.2	3.8	0.3	7
Total type 3 (n=2)	25.7	1.8	0.06	1.6	0.6	2.3
Average type 1 (n=4)	15.3	1.3	<0.1	1.2	<0.1	0.6
Average type 2 (n=3)	12.9	1.8	<0.1	1.3	0.1	2.3
Average type 3 (n=2)	12.9	0.9	<0.1	0.8	0.3	1.2

S4 Analysis of recycling barriers

Table 25: Basis elements for a barrier analysis to be investigated

<table>
<tr><td rowspan="2">Product related analysis</td><td colspan="3">Product design</td><td colspan="3">Material composition</td></tr>
<tr><td>Change in product design</td><td>Available product information or labeling</td><td>Dissipation through product design</td><td>Recycling conflict with other valuable or relevant materials</td><td>Complexity of material composition</td><td>Recycling conflicts with contaminants</td></tr>
<tr><td rowspan="4">Recycling chain related analysis</td><td colspan="6">Collection of end-of-life devices</td></tr>
<tr><td colspan="3">Collection rates of relevant devices</td><td colspan="3">Trends on collection rates</td></tr>
<tr><td colspan="3">Pre-processing</td><td colspan="3">End-processing</td></tr>
<tr><td>Mechanical liberation of target materials</td><td>Availability of identification and sorting technology</td><td>Complexity of metallurgical liberation</td><td>Separability after liberation</td><td colspan="2">End-refining channels available</td></tr>
<tr><td rowspan="2">Economy related analysis</td><td colspan="6">Economy</td></tr>
<tr><td colspan="3">Financial drivers for the recovery of target material</td><td colspan="3">Energy consumption and waste water/residues production</td></tr>
</table>

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